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(54) Method of forming opaque coloured areas in hydrogel contact lenses

(57) A method for opaquing and tinting selected areas of a hydrogel contact lens in which the lens is (a) masked and the unmasked area is contacted with a solution of a complex silver salt (e.g. silver ammonium nitrate), (b) the unmasked area is treated with a reducing agent (e.g. ascorbic acid or formaldehyde) to form particles of nacreous silver suspended within the lens, and (c) the lens is treated with a solution of a dyestuff (e.g. a reactive dye or vat dye) before or after steps (a) and (b).

Also claimed is a hydrogel contact lens containing silver in the form of a nacreous pigment present in substantially the whole thickness of the lens.

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METHOD OF FORMING OPAQUE COLOURED AREAS IN CONTACT LENSES

The present invention relates to a method of treating hydrogel contact lenses in order to colour areas which correspond to the iris of the wearers.

Contact lenses may require to be coloured in the iris areas either to mask eye disorders or lack of iris pigmentation or, more commonly, to change or enhance the appearance of the eyes. Merely tinting the lens by printing a dyestuff onto the selected area is not generally effective because the natural colour of the iris is normally readily apparent through the tinted lens. Often the resulting colouration when the lenses are worn gives a rather muddy effect rather than a desirable natural appearance. The difficulties of successfully producing an attractive result are generally increased where the natural colouration of the eyes is dark.

U.S. Patent No. 4558931 (Fuhrman) describes a method of producing contact lenses having coloured iris zones which utilises, as a starting material, a laminate consisting of alternate layers of coloured and water-white plastics material. By carefully machining the lens from the laminate in such a way that the iris zone is formed from the coloured layer, a lens having an internally coloured iris zone is formed. However, this method suffers from the disadvantage that it is laborious and it is difficult to coordinate the size of the iris area with the other desired parameters of the lens. This is particularly true in the case of hydrophilic lenses since

the machining step must be carried out on the laminate prior to hydration.

Proposals have also been made to mask the natural colour of the iris by precipitating opaquing materials within the desired areas of the lenses. One typical proposal of this kind is described in U.S. Patent No. 4,634,449, which discloses the precipitation of insoluble silver chloride within a hydrogel lens and suggests that this precipitate is ultimately reduced to silver particles by exposure of the treated lens to light. However, there are difficulties with known methods in ensuring that the opaquing agent is precipitated within the hydrogel and in achieving a natural effect.

According to the present invention there is provided a method of opaquing and tinting selected areas of a hydrogel contact lens especially those corresponding to the iris of the wearer, which comprises the following steps:-

(a) masking the lens and contacting the unmasked area with a solution of a complex silver salt,

(b) treating the unmasked area of the lens from step (a) with a solution of a reducing agent effective to reduce the complex silver salt to form particles of nacreous silver suspended within the lens, and

(c) treating the lens with a solution of a dyestuff before or after steps (a) & (b).

Preferably, the dyestuff is applied to the lens prior to the opaquing treatment. In the case of lenses based

on polyhema (polyhydroxyethyl methacrylate), this results in brighter and more contrasting colours than where the reverse procedure is employed.

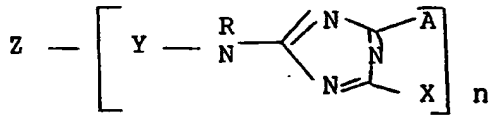
The conditions under which the silver is introduced into the lens and reduced to nacreous silver are important. The silver salt is used in the form of a complex salt, e.g. an ammonium or substituted ammonium salt. Apparently, this enables the silver salt to penetrate the hydrogel structure more effectively than a simple silver salt, such as silver nitrate. Also, the reducing conditions are of some significance. We have found that the choice of reducing agent is important. The preferred reducing agent is ascorbic acid. When a solution of ascorbic acid is employed the silver is readily reduced to a fine white, nacreous precipitate of silver particles. The ascorbic acid solution is preferably acidified, e.g. with sulphuric acid, to a pH within the range of 1 to 3, especially about pH2.

Generally speaking, other known reducing agents for silver are ineffective or less effective than ascorbic acid. For example, reducing sugars and ionic reducing agents are unreliable in reducing the salt to silver within the hydrogel. Formaldehyde may however be employed satisfactorily.

The preferred procedure for the tinting and opaquing operation is as follows. A swollen hydrophilic lens is placed in a holder which masks the pupil and sclera areas, but allows access to the iris area. One suitable

apparatus of this kind is described in U.K. Patent Specification No 2130507. A solution of the dyestuff is brought into contact with the iris area. Vat dyes may be employed but any non-toxic dye which has an affinity for the hydrogel may be used.

Preferably, however, reactive dyes which react with the hydroxyl groups present in most hydrogel polymers are used. Particularly preferred dyes are those having the structure



where A is halogen especially chlorine or O-B or N-B where B is a hydrocarbon radical or substituted hydrocarbon

n is a whole number

R is hydrogen, alkyl, aralkyl or cycloalkyl

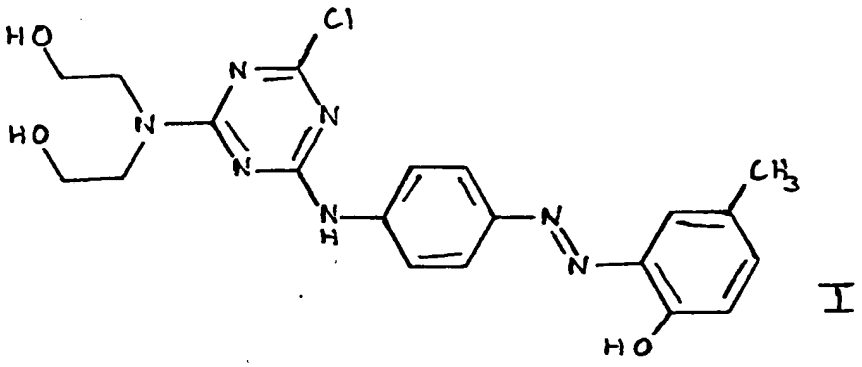
X is halogen, especially chlorine

Y is a direct link or a divalent bridging link

Z is a chromophore, especially a phthalocyanine radical, or an azo containing radical

Some such compounds are disclosed in GB 805 562, GB 785 222, GB 785 120 and GB 774 925.

A number of these dyestuffs are available under the 'Procion' and 'Procinyl' trade marks from ICI. Examples of such dyestuffs are Procinyl Yellow GS(I) and Procion Brilliant Red M-2BS(II).



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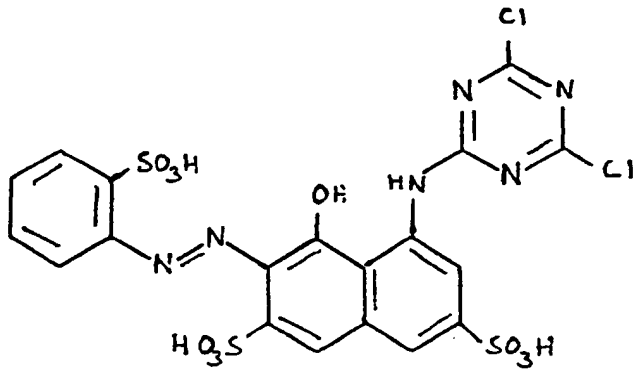

II

The most preferred dyestuffs are generally those having a 2-amino-4-chlorotriazinylamino radical and those having a 2,4-dichlorotriazinylamino radical.

In order to assist penetration of the vat dye into the hydrogel, the dye is preferably dissolved in a water miscible solvent or in a solution of solvent/water mixture. Suitable solvents include aliphatic alcohols. The solution of the vat dye in its leuco form is left in contact with the lens for about 2 minutes. After washing with water, the dye is developed in conventional manner using an acidified oxidising agent, such as an aqueous solution of sodium nitrite acidified with sulphuric acid. The depth of colour can be controlled by varying the dy concentration, temperature and length of treatment.

Following the tinting treatment, (and washing to remove the dye developing solution), the lens is subjected to the opaquing procedure. A water-soluble silver complex salt is prepared by adding ammonia to a dilute aqueous solution of silver nitrate. A concentration of about 0.02 to 1% of silver nitrate (e.g. about 0.05 to 0.1%) has been found to be suitable. Initially, a precipitate of silver hydroxide is formed which then redissolves in further ammonia to form a solution of silver ammonium nitrate. The resulting solution is then brought into contact with the iris area of the lens for a period of about 1 minute and then the excess is washed off. Finally, the lens is treated with a solution of the reducing agent, preferably an acidified solution of ascorbic acid for a contact period of about 2 minutes. All treatment steps were carried out at about 20°C. It has been found that, even when using the dilute silver salt solutions indicated above, the technique described herein, involving the formation of a silver ammine complex salt, enables a satisfactory opaquing level to be achieved.

After washing off excess reducing agent, the lens can be removed from the masking apparatus. Examination of sectioned lenses treated in accordance with the invention shows that the silver forms a nacreous pigment which is present throughout the major part of the thickness of the lens and appears to be concentrated in the central portion. The dye however, forms a relatively superficial colouring in the front surface layer of the

lens which has been contacted with the dye solution and is generally restricted to about 10% of the thickness of the lens. Apparently, the silver passes through the dyed layer and the result is a brightly coloured opaqued iris area. The degree of opaquing can be controlled (e.g. by limiting the initial concentration of silver to about 0.02 to 0.05%) so that when the lens is worn, the corona of the eye of the wearer can be seen through the coloured iris area of the lens and thus gives a convincingly natural appearance.

Surprisingly, despite the fact that the silver salt solution penetrates substantially throughout the thickness of the lens, there appears to be little bleeding of pigment or colour laterally into the pupil or sclera areas.

Opaqued and tinted lenses produced in accordance with the invention can be sterilised by autoclaving without loss of pigment or colour.

As indicated above, the procedure can be modified by substituting a 'Procion' dye for the vat dye. Procion dyes are developed by treatment with sodium hydroxide solution and in common with the vat dyes, tend to be restricted to the surface layer or layers of the lenses.

In the case where a Procion dye is used to tint the lens, a convenient procedure is to contact the lens with a dilute solution of the selected Procion dye (typically a concentration of 0.5 to 1.0%) in de-ionised water or in a mixture of de-ionised water and a suitable water-miscible

solvent, e.g. 1,2-dimethoxy ethane. Selective contact of the iris part of the lens with the dye solution is effected using a holder such as described in U.K. Patent Specification No. 2130507. The dye is fixed by contacting the lens with a 0.1N solution of sodium hydroxide. The tinted lens can then be subjected to the opaquing treatment using a complex silver salt and reduction with ascorbic acid as described above.

Lenses may be tinted with a dye and held in stock pending application of the opaquing treatment.

The method of the present invention has been carried out satisfactorily on a variety of hydrogel lens polymers including polyhema and copolymers of N-vinyl pyrrolidone and hydroxyethyl methacrylate, e.g. as described in U.K. Patents Nos. 1385677; 1475605; 21307430 and 2138831. Other patents describing the preparation of contact lenses include U.S. Patents Nos. 3220960; 4208364 and 4208365. The process of the present invention is applicable to the production of plano contact lenses, which provide no vision correction, as well as to ophthalmic contact lenses. The term 'contact lens' is therefore used in this specification to include both plano and opthalmic contact lens.

CLAIMS

1. A method of opaquing and tinting selected areas of a hydrogel contact lens, which comprises the following steps:-

(a) masking the lens and contacting the unmasked area with a solution of a complex silver salt,

(b) treating the unmasked area of the lens from step (a) with a solution of a reducing agent effective to reduce the complex silver salt to form particles of nacreous silver suspended within the lens, and

(c) treating the lens with a solution of a dyestuff before or after steps (a) and (b).

2. A method of opaquing and tinting selected areas of a hydrogel contact lens according to claim 1 wherein the lens is treated with a solution of a dyestuff before steps (a) and (b).

3. A method according to claim 1 or claim 2 wherein the complex silver salt is an ammonium or substituted ammonium salt.

4. A method according to any one of claims 1 to 3 wherein the reducing agent is ascorbic acid or formaldehyde.

5. A method according to claim 4 wherein solution of the reducing agent is an ascorbic acid solution having a pH within the range 1 to 3.

6. A method according to any one of claims 1 to 5 wherein the dye is a vat dye.

7. A method according to any one of claims 1 to 5 wherein the dye is a reactive dye.

8. A method according to claim 8 wherein the dye has a 2-amino-4-chlorotriazinylamino radical or a 2,4-dichlorotriazinylamino radical.

9. A method of opaquing and tinting selected areas of a hydrogel contact lens substantially as described herein.

10. A hydrogel contact lens containing silver in the form of a nacreous pigment present in substantially the whole thickness of the lens.

11. A hydrogel contact lens as claimed in claim 10 wherein the silver is concentrated in an annulus surrounding the central portion of the lens and corresponding approximately to the iris of the intended wearer.

12. A hydrogel contact lens as claimed in claim 10 or claim 11 additionally comprising a dye.

13. A hydrogel contact lens as claimed in claim 12 wherein the dye is restricted to a zone not more than 10% of the thickness of the lens.

14. A hydrogel contact lens as claimed in any one of claims 11 to 13 wherein the dye has a 2-amino-4-chlorotriazinylamino radical or a 2,4-dichlorotriazinylamino radical.

15. A hydrogel contact lens as claimed in any one of claims 10 to 14 wherein the lens is plano.

16. A hydrogel contact lens substantially as described herein.